

Studies of Pitting Interactions Using Response Surface Methodologies

J. S. Lee¹, M. Chen², M. F. Leung², S. Lin², Y. Xue²
C. M. Mastrangelo², R. G. Kelly

¹Department of Materials Science and Engineering

²Department of Systems Engineering

University of Virginia

116 Engineer's Way

Charlottesville, VA 22904-4745

Localized corrosion sites establish concentration and electrical gradients in the solution surrounding the site. The influence of one pit on the stability of another has become of increasing interest in recent years in both corrosion science and engineering. In theory either of the two types of fields (chemical and electrical) can influence the formation and stability of the second pit. Although many experimental measurements have been made to probe the importance of each of these phenomena, computational work aimed at understanding the relative importance of each has been more limited.

Standard statistical models have long been used to assist in both the design and analysis of corrosion experiments. Recent advances in the field of response surface methods were used to both efficiently select and then analyze the results of computational experiments aimed at beginning to map the conditions under which a second pit can propagate.

A two-dimensional, time transient mass transport model was used in which two pits were initiated and allowed to grow. Simplified material behavior was assumed; if the pH above a site were above a transition pH, the site dissolved at a passive rate (in all cases 10 $\mu\text{A}/\text{cm}^2$), whereas if the pH above the site were below the transition pH, the site dissolved at an active rate (between 1 and 1000 mA/cm^2). Pits were initiated by forcing the pH of a region to an initial pH below the transition pH. The model determined if, four minutes after the second pit was initiated, both pits were still stable (i.e., the rate of change of pH was not positive above the sites).

Based on these simulations, two linear models of the stability of the second pit were developed. It was found that the three most important factors were the assumed transition pH (range studied 2.5 to 4), the starting pH of the second pit (range studied 1 to 3), and the relative dissolution rate of pit 2. A linear model based on only these three variables had an R^2 value of 0.74. The model can be described as:

$$\frac{d(\text{pH})}{dt} = 0.56 - 0.21(\text{DissRate}) - 0.33(\text{TranspH}) + 0.38(\text{Pit2pH}) - 0.33(\text{TranspH})(\text{Pit2pH})$$

Increasing the complexity of the equation by including additional interaction terms as well as the initial pH of pit 1 leads to a linear model with ten terms and an R^2 value of 0.92 as shown in Figure 1.

Of equal interest was the determination that neither the pit separation (range studied 0.4 to 1.2 cm) nor the time delay before the second pit is initiated (range studied 300-2100 sec) were predictive in the stability of the second pit under the conditions studied.

Further discussion of the implications of these results as well as the effects of potential dependent boundary conditions will be presented.

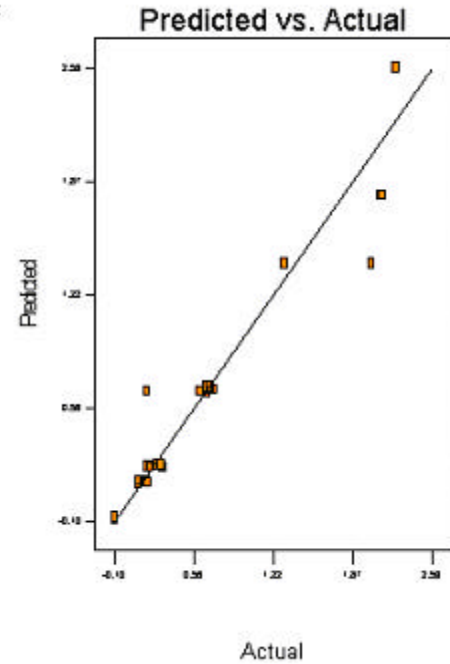


Figure 1: Predicted time-rate of change of pH over the second pit at four minutes vs. actual time-rate of change of pH from computational model.